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IN X-RAY IRRADIATED CdS SINGLE CRYSTALS

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PRODUCTION AND ANNEALING OF INTRINSIC DEFECTS  
IN X-RAY IRRADIATED CdS SINGLE CRYSTALS\*

by

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ABSTRACT

X rays (300 keV) have been used to produce changes in the defect structure of (1) "pure" single-crystal platelets of CdS and (2) platelets which have been pre-heat-treated in the vapor of one of its components. The changes were studied by means of the spectral distribution of photocurrent and T. S. C. curves. All measurements were made in ultrahigh vacuum ( $10^{-10}$  Torr). The damage produced annealed at temperatures between  $100^{\circ}$  and  $150^{\circ}\text{C}$ . The reproducible damage-annealing cycle has been explained in terms of intrinsic defects produced in the sulfur sublattice. Damage-annealing cycles for crystals pre-heat treated in Cd or S vapor (stoichiometry shift) provide additional confirmation for the proposed model.<sup>1</sup>

<sup>1</sup> K. W. Böer and J. C. O'Connell, International Symposium on Luminescence, Budapest, 1966.

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The knowledge of the defect structure and of its connection with the level distribution in the band gap is an important prerequisite for the thorough understanding of luminescence and photoconductivity of solids. In a previous paper\*, an attempt was made to give some contributions to this question for cadmium sulfide by analyzing the results of x-ray damage and annealing done under ultra high vacuum conditions using the spectral distribution of photoconductivity and thermally stimulated current measurements, hereafter called TSC curves.

It has been shown that the threshold for x-ray damage observed by change in electrical properties of CdS at room temperature lies between 250 and 300 keV. For a 300 keV irradiation at room temperature, a typical damage-annealing cycle is given in Figure 1.

1) is before and 2) is after x-ray damage, 3) after waiting several days at room temperature and after annealing at 4) 100°C and 5) 150°C. This sequence will be used for all reported cycles. The model proposed, which is the most economical and yet explains all the results is as follows. The primary defect produced by x-ray damage is the displacement of a sulfur atom from its lattice site in the neighborhood of an already existing crystal defect such as the crystal surface, a low angle grain boundary, etc. The presence of the

\* "X-ray Damage & Annealing of These Defects in CdS Single Crystals" Luminescence Symposium Verl. K. Thiemig, K. G., Munich (1966) by K.W. Böer, J.C. O'Connell & R. Schubert

resulting sulfur vacancy gives rise to a level 0.5 eV below the conduction band as determined by the growth of a TSC peak at 300°K. The remaining changes in the damage cycle are given in terms of a change in electron lifetime as will be seen in Figure 2. Here the spectral distribution of photoconductivity corresponding to the same damage-annealing cycle are given. At room temperature some of the sulfur vacancies produced associate with oppositely charged defects and form recombination centers, thereby reducing the photoelectric gain factor as is evident by the wavelength independent reduction of the photosensitivity. These associates continue to form if the crystal remains at room temperature. A heat treatment at 150°C for one hour is sufficient to dissociate the associates and reunite the sulfur vacancies with the displaced sulfur, thus returning the crystal essentially to the pre-damaged state.

It is the purpose of this paper to present further experimental material on x-ray damage at liquid nitrogen temperature and on crystals pre-treated in sulfur vapor which supports this model.

The following experimental investigations were done on undoped CdS single crystal platelets with four evaporated gold chromium electrodes (two potential electrodes are used to correct for possible barrier layer influence). During the whole set of measurements the

crystals were kept at a vacuum of better than  $5 \times 10^{-10}$  torr.

For x-ray irradiation the crystals were exposed to the unfiltered output of an x-ray tube at 300 keV, 7.5 ma for two hours (the anticathode-crystal distance was about 45 cm.).

Figure 3. If the x-ray damage is done at liquid nitrogen temperature, there is no observable change in photosensitivity after x-ray irradiation as long as the crystal is kept at low temperature. This is to be expected if no additional recombination centers are created. Therefore, the diffusion process by which the associates acting as recombination centers are formed is frozen-in at liquid nitrogen temperature. However, as will be seen from the TSC curves, the primary displacement of a sulfur atom and the creation of a sulfur vacancy can take place at this temperature. After increasing the temperature to room temperature, associate formation can take place and therefore a decrease of photosensitivity is expected. Annealing at  $100^{\circ}\text{C}$  essentially returns the crystal to its original state.

Figure 4. The set of TSC curves for the liquid nitrogen temperature x-ray damage cycle looks very similar to the damage cycle measured at room temperature. During the run of the TSC curve there seems to be some diffusion already taking place above  $150^{\circ}\text{K}$  since from here on the

TSC curve directly after irradiation lies markedly below the TSC curve before irradiation. At temperatures above  $250^{\circ}\text{K}$ , the TSC curve shows an increased amount of sulfur vacancies due to x-ray damage. After waiting at room temperature the TSC curve shifts toward lower values because of further associate formation.

Figure 5 shows the relative change of photosensitivity before and 5 days after each x-ray cycle. After running several damage-annealing cycles on the same crystal it is apparent that the amount of damage decreases from cycle to cycle for x-ray damage at room temperature while for liquid nitrogen temperature such a change was not observed. The decrease of the sensitivity of CdS to further damage is due to an incomplete annealing i.e. part of the displaced sulfur remains at the surface or at small angle grain boundaries after annealing.

Figure 6. If the CdS crystal was heat treated in a sulfur atmosphere at  $750^{\circ}\text{C}$  for one hour before exposing it to damage at 300 keV, there was no observable change in photosensitivity after the damage (curve 1 and 2). However, after vacuum heat treatment of the same crystal at  $300^{\circ}\text{C}$ , the crystal became sensitive to x-ray damage in the same manner as the untreated crystals. The sulfur treated crystals already have an excess of sulfur available, especially at the surface, to saturate areas where defects are produced and no measurable damage occurs.

The vacuum heat treatment causes a partial evaporation of this excess and a return towards untreated crystal behavior.

The effects of x-ray damage on cadmium sulfide crystals pre-treated in cadmium vapor are now being studied. These crystals tend to be in a high conductivity state after irradiation (i.e. higher than the photocurrent maximum before irradiation). This however, is due to temporary sensitization of the crystal which can be destroyed by exposure to band gap light. This is due to a photochemical reaction which masks x-ray damage induced changes of electrical properties.

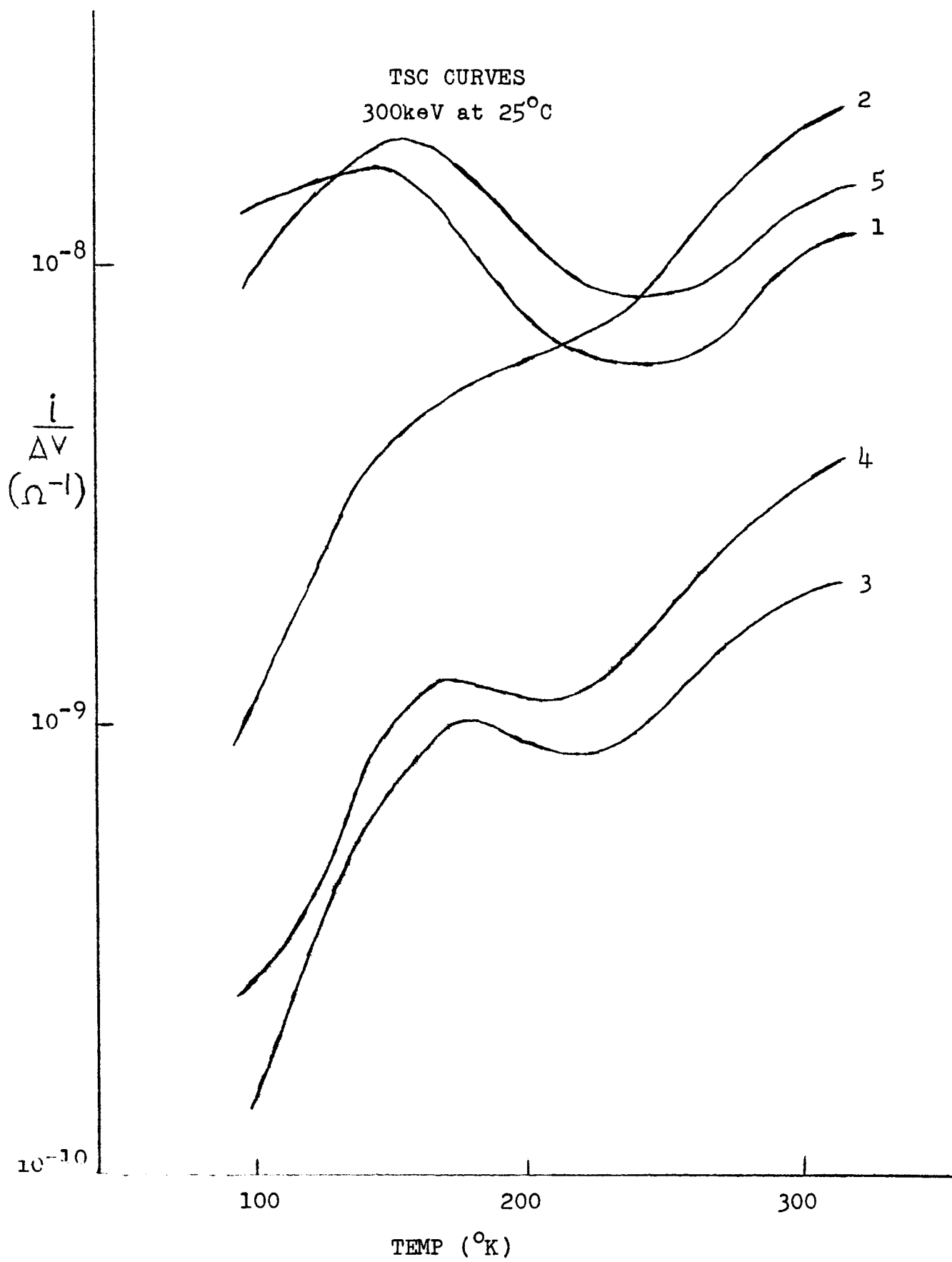


FIGURE 1



SPECTRAL DISTRIBUTION OF  
PHOTOCURRENT  
300 keV at 25°C

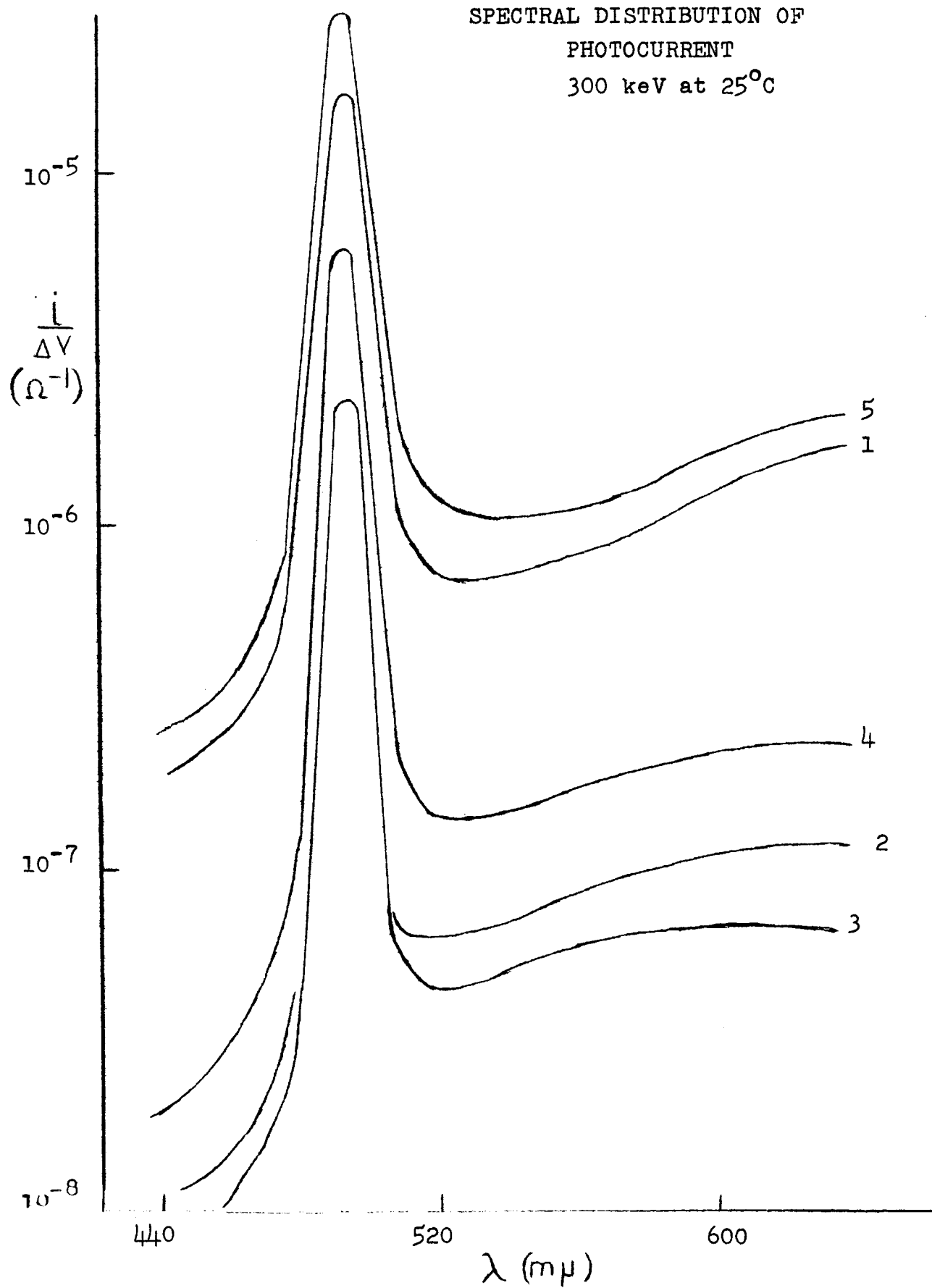


FIGURE 2

SPECTRAL DISTRIBUTION OF PHOTOCURRENT  
300keV at  $-180^{\circ}\text{C}$

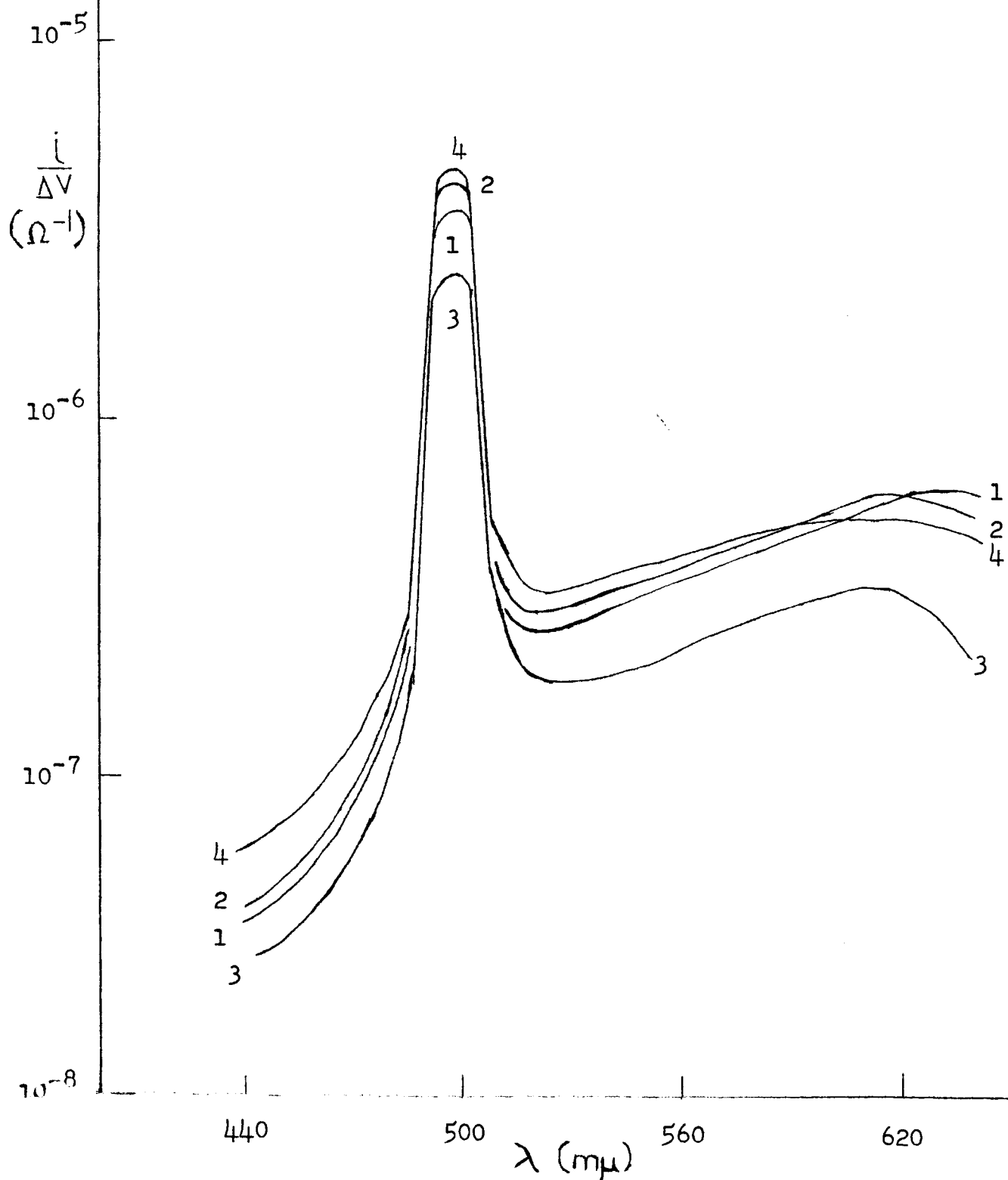


FIGURE 3

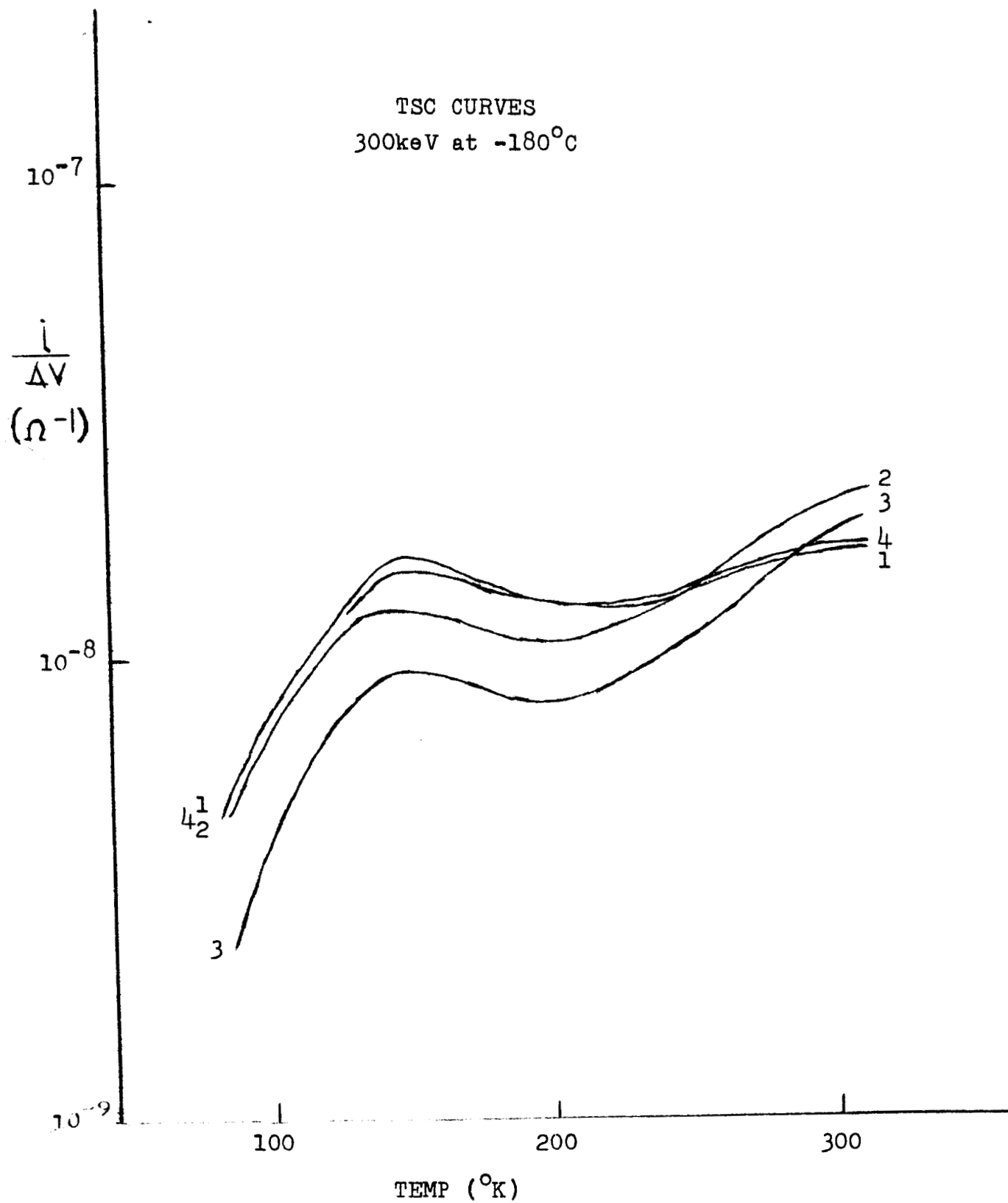
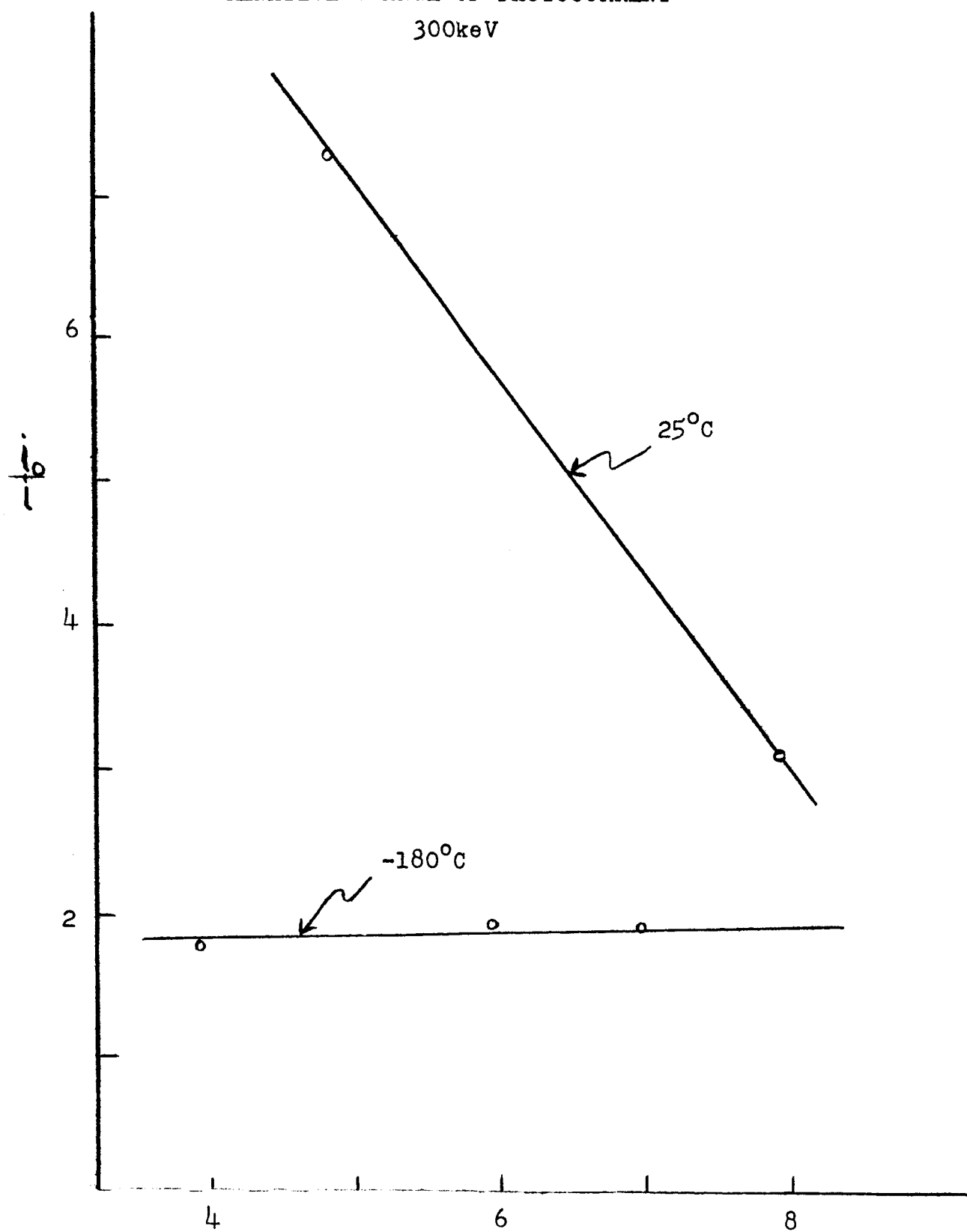


FIGURE 4

RELATIVE CHANGE OF PHOTOCURRENT  
300keV



NO. of CYCLES  
FIGURE 5

SPECTRAL DISTRIBUTION OF PHOTOCURRENT  
300keV at 25°C

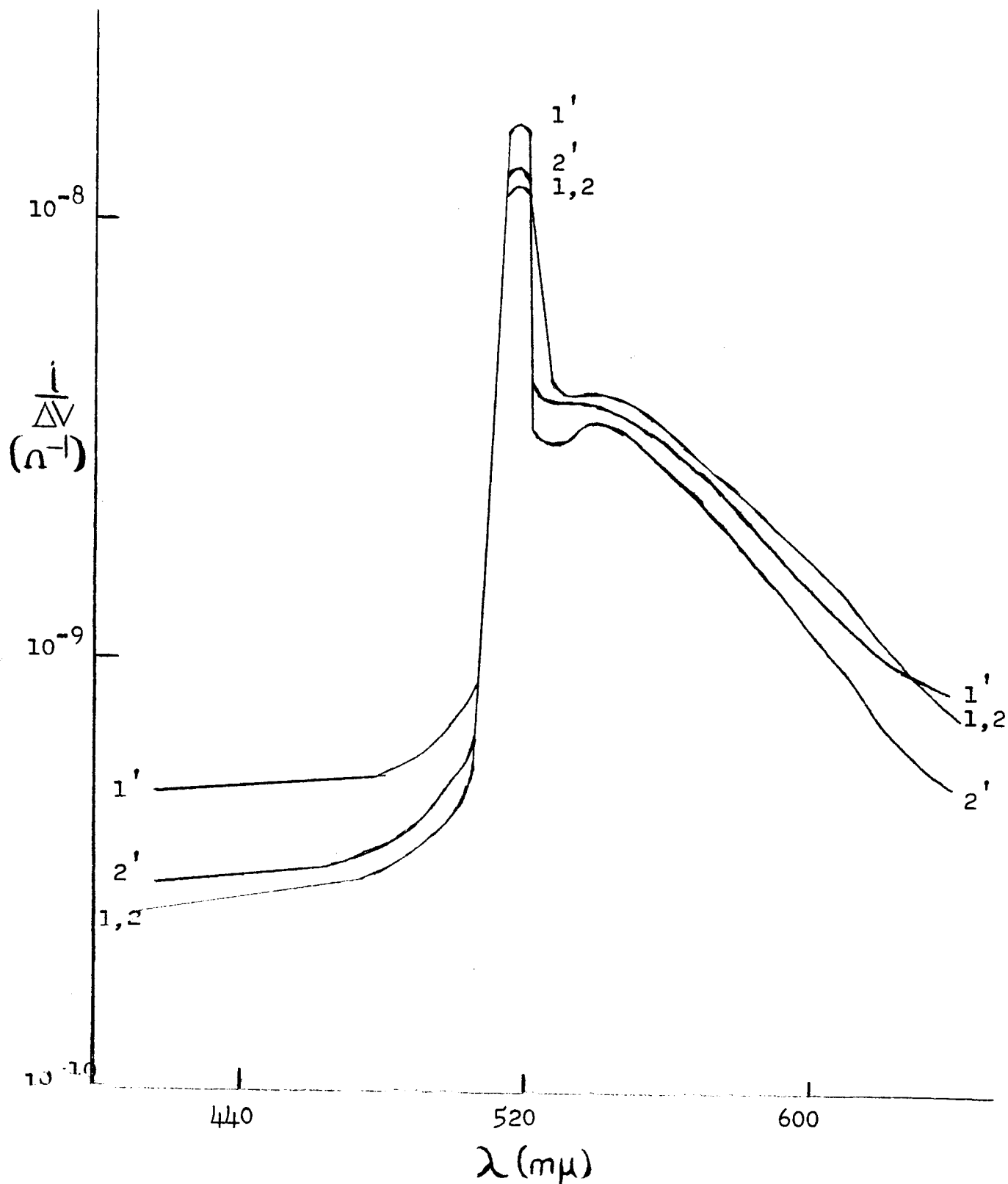


FIGURE 6